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Platy α -SiC Single Crystals Grown From Solvent Silicon

シリコン溶液から成長させた板状の α -SiC 単結晶

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Translated from Ceramic Society of Japan: Journal (YOGYO KYOKAI-SHI 瓷業協会誌.),
Tokyo 79(8):259-263 [72-6 (Emm-72-275)]

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AIR FORCE SYSTEMS COMMAND
United States Air Force



Unclassified
Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Air Force Cambridge Research Laboratories (IQS) L.G. Hanscom Field Bedford, Massachusetts 01730	2a. REPORT SECURITY CLASSIFICATION Unclassified 3a. GROUP
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1. REPORT TITLE

PLATY α -SiC SINGLE CRYSTALS GROWN FROM SOLVENT SILICON

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Scientific. Special

5. AUTHOR(S) (First name, middle initial, last name)

Yoshizo Inomata
Zenaburo Inoue
Mamoru Mitomo

6. REPORT DATE 12 April 1972	7a. TOTAL NO. OF PAGES 16	7b. NO. OF REFS 14
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8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S) AFCRL-72-0265
---------------------------	--

b. PROJECT, TASK, WORK UNIT NOS. N/A

c. DOD ELEMENT N/A

d. DOD SUBELEMENT N/A

9a. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
Translations No. 98

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES Translation: From Ceramic Society of Japan: Journal (Yogyo Kyokai-Shi) Japan, Vol. 79, No. 8, pp. 259-263, 1971.	12. SPONSORING MILITARY ACTIVITY Air Force Cambridge Research Laboratories L.G. Hanscom Field Bedford, Massachusetts 01730
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13. ABSTRACT

Platy α -SiC crystals of 2-3 mm in diameter were grown in high-density graphite crucibles with high-purity solvent silicon after 5 hours' heating at 2200°C. The crystals obtained consisted mainly of 6H. When compared with crystals grown by sublimation, the probability of forming twins with a 70° 30° angle between the bases was small. Some of the crystals contained very thin silicon layers, but these regions were generally localized and fine scattered carbon particle inclusions such as seen in crystals prepared by sublimation were not observed.

The relation between the polarity of the basal faces and their growth rate was studied by chemical etching, and it is suggested that there is a reverse relation between the crystals grown from solvent silicon and those prepared by sublimation.

DD FORM 1 NOV 68 1473

Unclassified
Security Classification

Unclassified
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Silicon carbide						
Crystal growth						
Polytpism						
Growth structure						

... Unclassified
... Security Classification

II

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Platy α -SiC Single Crystals Grown From Solvent Silicon

1. INTRODUCTION

Relatively large α -SiC single crystals prepared by sublimation (Lely, 1955) often contain fine carbon particles (Inomata et al, 1970a).

In the present experiments use was made of solvent silicon to grow α -SiC crystals free of carbon particle inclusions. The characteristics of the crystals are discussed and compared with those produced by sublimation.

The temperature was set at 2200°C to realize a fast growing speed. This temperature is the highest limit for obtaining a stable performance, since the boiling point of silicon under one atmospheric pressure is in the neighborhood of 2300°C.

Sizable crystals free of carbon particle inclusions which is uncommon to those grown by sublimation were obtained. However, the physical characteristics of the crystals, such as purity, are not investigated. It should be noted here that the growth of β -SiC (3C) by a similar technique has been reported by Nelson et al (1966).

2. EXPERIMENTS

The method of growth is similar to that described in the papers by Inomata et al (1969a; 1969b) except that S.D.H. (bulk density > 1.80) manufactured by the Nippon

(Received for publication 12 April 1972)

Carbon Co., Ltd. was used as raw material for the graphite crucibles. The S.D.H. underwent the same high-purity treatment as that usually given to graphite used as a moderator. The crucibles are of inner diameter 25 mm, wall thickness 15 - 20 mm, and depth 50 - 60 mm. Heating was accomplished using both a graphite resistance (Inomata et al, 1968a) and a high-frequency induction furnace.

If the crucible were made of material similar to that employed for the slowing-down of atomic piles, the solvent silicon would seep out through the wall and could not be retained for a long period of time. The crucibles used in the present experiments held the solvent well.

Approximately 50 grams of high-purity silicon (purity above 5N) made by the Chisso Co., Ltd. was placed in a crucible, vacuum-substituted in a furnace at room temperature under one atmosphere of high-purity argon ($N_2 < 5$ ppm), heated to 2200°C, kept at this temperature for several hours, and then was cooled rapidly. The crucible was taken out after cooling, and crystals were collected for observation after silicon was removed with a 1:1 mixture of nitric and hydrofluoric acids.

Heating was attempted in a vacuum also, but when the temperature exceeded the melting point of silicon in a vacuum of $10^{-4} - 10^{-5}$ Torr, the graphite crucible was often damaged. Experiments may be carried out safely with a crucible of appropriate form and thickness, but special precautions must be taken since the furnace is also liable to damage.

Even when high-density graphite is used, the solvent silicon leaks out through the gap between the crucible and the lid, making it difficult to perform lengthy experiments. The present trial lasted 5 hours.

3. RESULTS

3.1 Crystals

Figure 1 shows crystals which were grown while the temperature was maintained at 2200°C for 5 hours and the thermal gradient in the crucible was such that the bottom portion was approximately 20°C lower than the middle portion. The well-shaped crystals obtained under these conditions are mostly of the hexagonal platy α -type, and in general they are thinner than those obtained by sublimation. One of the features is the small probability of forming

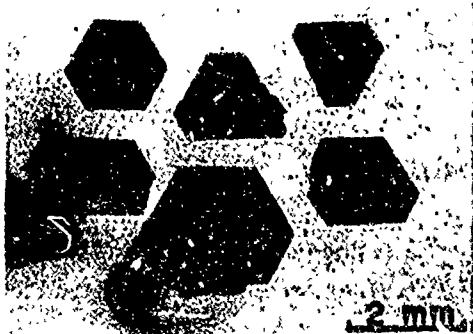


Figure 1. Platly α -SiC Crystals Grown From Si Melts at 2200°C for 5 Hours

wurtzite-type twins whose angle between the bases is approximately $70^{\circ}30'$. Among the platy crystals are some whose basal planes are slightly curved. Although not evident in the figure, there are two crystals which exhibit Newton rings between them and the glass plate.

Figure 2(a) is a dark field photomicrograph of a relatively large crystal obtained using the solvent silicon technique. The scattered elements in the crystal are accidental dust particles which have not been removed. No inclusions such as those observed in crystals obtained by sublimation were found. Figure 2(b) is a typical example of a crystal obtained by the same technique, which contains thin silicon layers. The small isolated area to which the arrow points is one of the silicon layers. Since this area is transparent and appears brownish under natural light, it should be a very thin layer of approximately 100 \AA . Similar inclusions were often observed in other prepared crystals, particularly in larger ones.

Figure 3 shows an extreme case of this phenomenon. The crystal was grown in one hour in a crucible with a slightly larger thermal gradient. The crystal has striations since it was grown at a greater speed than the ones shown in Figure 2. The structure parallel with the crystal edge is not on the basal plane, but exists within the crystal. Therefore, it may be concluded that during growth the silicon solvent phase was being absorbed inside. Such a crystal, however, tends to develop cracks within because of the expansion which takes place at the time of silicon solidification. This is observed near the center of the crystal in the figure. The dark area on the right is unremoved silicon residues.

β -SiC is formed in the initial stage of crystallization in this process just as in the sublimation process. As a result, these initial crystals were often found to remain epitaxially on the platy α -type crystals (Komata et al, 1968b).

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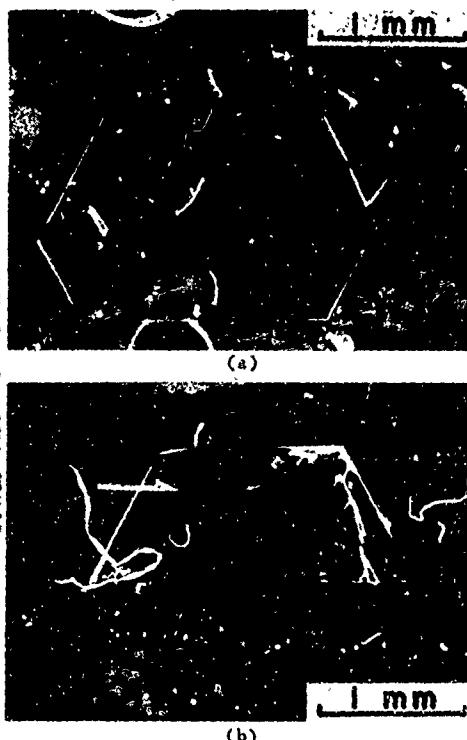


Figure 2. Dark Field Photomicrographs of Two Typical Examples. The bright dots in photograph (a) are accidental dust particles which are of no significance; the arrow in photograph (b) points to a thin silicon layer

3.2 Crystal Polytypes

Table 1 gives results of an attempt to identify by oscillational photography the polytypes of platy crystals grown at 2200°C in 5 hours. The polytypes are listed in the descending order of the diffraction spot intensity. Lp denotes a long-period structure. A circle in the diffuse streak (stacking disorder) column indicates a crystal in which distinct stacking disorders were found. The two observed features are (1) the predominance of the 6H type and (2) the existence of stacking disorders in many of the crystals.

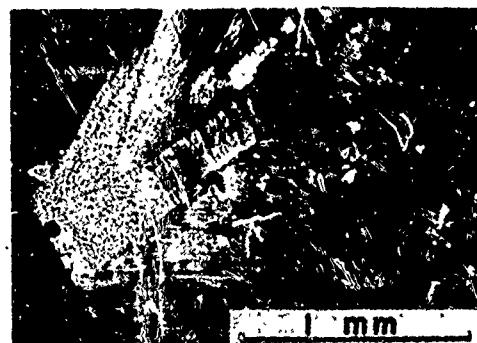


Figure 3. Crystal Grown With a Larger Temperature Gradient at 2200°C in One Hour. The crystal has striations and silicon layer inclusions. The dark area on the right are silicon residues

Table 1. Structure of SiC Crystals Grown From Silicon Melt at 2200°C in 5 Hours

No.	Structure	Diameter (mm)	Thickness (mm)	Thick. Dia.	Stacking Disorder	Color*
1	6H	2.5	0.01	0.004	O	G
2	3C + 6H	2.4	0.04	0.017	O	YG
3	6H + 3C + Lp.**	1.9	0.03	0.016	O	YG
4	6H	1.7	0.015	0.009	O	G
5	6H + 66R (?)	1.5	0.015	0.010	O	G
6	6H + 3C	1.4	0.02	0.014	O	YG
7	6H + Lp.	1.4	0.02	0.014	O	G
8	6H	1.3	0.015	0.012	O	G
9	6H	1.2	0.015	0.013	O	G
10	6H	1.2	0.015	0.013	O	G
11	6H	1.2	0.015	0.013	O	G
12	6H	1.2	0.015	0.013	O	G
13	6H	1.1	0.03	0.027	O	G
14	6H	1.1	0.01	0.009	O	G
15	6H	0.7	0.02	0.029	O	G

* G and YG stand for green and yellowish green respectively.

** Lp. means a structure having a long c-period.

Since graphite was used for the crucible and high-temperature degassing was not performed, crystals were tinted generally by forming solid solutions with nitrogen.

Since 6H exhibited a slight bluish green color and β -SiC its characteristic yellow color, it was relatively easy to distinguish the epitaxial residues described above. Crystal no. 2 listed in the table corresponds to such a case.

3.3 Basal Surface Growth

Figure 4 shows results of differential interference observation of the (0001) face of a particularly large crystal. The crystal displays clear growth patterns. Figure 4(a) shows a fastly grown face on which numerous growth spirals are observed. Figure 4(b) is complicated because a reflection from the (a)-face is superimposed. However, it was confirmed that the pattern with high contrast corresponds to dissolution, judging from the height and curvature of the steps studied by the phase difference technique. The (a)-face also has a reflection from the (b)-face superimposed on it.

Obviously, the cooling process affected the growth and dissolution. However, if we recall that a cooling process increases the degree of supersaturation of a solution, then it is logical to consider that even under normal conditions the same relationship existed for the growth speeds of the faces shown in Figure 4 although the conditions for them were different.

Figure 5 shows two different parts of the same crystal which was chemically etched for one hour with NaOH dissolved at 400°C. Figure 5(a) shows a fastly grown face. No pits appear on this face, but triangular pits form on the opposite (b)-face.

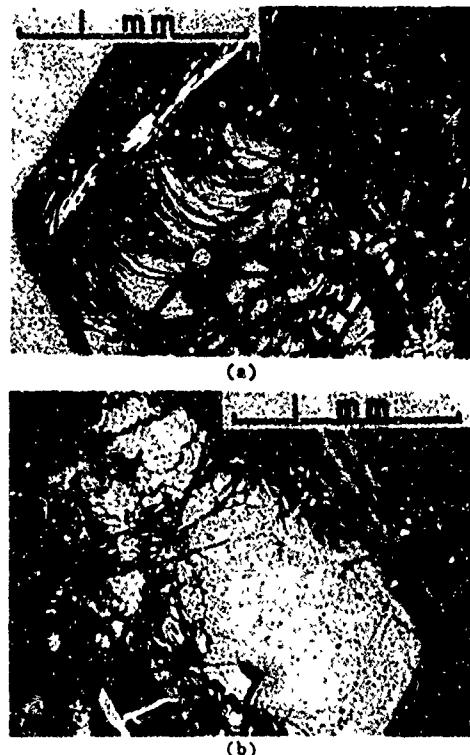


Figure 4. Surface Structures of a Crystal Grown With a Large Temperature Gradient. Face (a) shows numerous growth spirals; the opposite face (b) shows a pattern of dissolution

In crystals prepared by sublimation, the etching conditions stated above tend to produce etch pits on the fastly grown face (Inomata et al, 1968c). The situation is reversed in the present case. The shape of the etch pits in Figure 5(b) indicates that the face which shows dissolution possesses layers corresponding to those on the (111) face of β -SiC.

4. DISCUSSION

4.1 Inclusions in Crystals

It was proposed that α -SiC crystals prepared by sublimation generally include fine carbon particles (Inomata et al, 1970a), but there was a slight ambiguity about the conclusion that the inclusions are carbon particles. The fact that crystals obtained here did not show such inclusions supports this conclusion.

The reason why silicon inclusions resulting from the solvent method and carbon inclusions from the sublimation technique exhibit marked differences in their distributions is that the former is in the liquid phase under the growth conditions whereas the latter tends to be in the solid phase.

Since inclusions in a crystal obtained by sublimation are very fine and scatter throughout the crystal, they are usually very difficult to observe. However, silicon inclusions are generally localized, as shown in Figure 2(b), and can easily be observed.

Carbon particle inclusions in crystals are great obstacles in constructing p-n junctions (Canepa et al, 1964). Since defects in crystals grown from solvent silicon are easily detected, the parts containing these defects should easily be removed.

4.2 Structural Characteristics

It was mentioned in Section 3.2 that the crystals obtained in the present experiments often contain stacking disorders and that there is a high probability of 6H formation.



(a)



(b)

Figure 5. Photographs of Two Different Parts of the Same Crystal (Figure 4) After Being Etched in Molten NaOH at 400°C For One Hour. Face (a) showed a higher growth rate

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When a SiC single crystal is grown without using seeds the formation and growth of α -SiC usually follow the initial crystallization of β -SiC. However, if the growth temperature is above 1600°C, the type that is most easily formed from β -SiC is 6H, and this tendency is more pronounced at higher temperatures (Inomata et al, 1969c; 1970b). This process of structural transformation accompanying crystal growth is described in Table 1 (Inomata et al, 1968b).

The 15R type which usually tends to coexist with 6H was not observed probably because this type could be grown easily in the neighborhood of 2200°C only if it started with the 6H twin structure with a 70°30' angle between the bases. Many of the platy crystals obtained in the present experiments did not contain this type of twins.

It was stated in Section 3.3 that parts of the basal surface had dissolved. This fact suggests that the initially crystallized parts will eventually disappear if the growth time is lengthened. Therefore, removal of the initially crystallized β -SiC and the regions containing stacking disorders seems possible during growth.

Experience shows that when the degree of supersaturation of the atmosphere during crystal growth is low, the above-mentioned transformation process appears to terminate in a relatively early stage of the growth. Therefore, changing the temperature gradient inside the crucible from the beginning to the end of the growth process may be an effective way of obtaining α -SiC single crystals with a nearly perfect structure.

4.3 Basal Surface Growth Speed

For tetrahedral binary-compound crystals, many arguments have been reported on the difference in the growth speed and structure between the two basal surfaces whose polarities are different (Brack, 1965; Komatsu, 1969). However, the effect of changes in the external conditions has not been well understood.

Although the results described in Section 3.3 were only one example concerning SiC, they show that crystals are strongly influenced by the environment in which they are placed. This may be attributed to the fact that the gas phase composition in the sublimation process is usually biased away from the equilibrium toward the carbon side (Inomata et al, 1970a), whereas in the solvent process crystals grow under overwhelmingly silicon-rich conditions.

Clear conclusions cannot be drawn since the present investigation was carried out on a limited number of crystals; however, to compare polarities and growth speeds, it seems necessary to consider the compositions in the gas and liquid phases, and the relationship between the microscopic temperature distribution inside the crystal and the environment.

5. SUMMARY

Platy α -SiC crystals of 2 - 3 mm in diameter were grown in high-density graphite crucibles with high-purity solvent silicon after 5 hours' heating at 2200°C. The crystals obtained consisted mainly of 6H. When compared with crystals grown by sublimation, the probability of forming twins with a 70°30' angle between the bases was small. Some of the crystals contained very thin silicon layers, but these regions were generally localized and fine scattered inclusions such as seen in crystals prepared by sublimation were not observed.

The etching tendencies for the two fastly grown basal faces with opposite polarities are found to be different. The tendencies for crystals grown from solvent silicon are the reverse of those for crystals prepared by sublimation.

Acknowledgments

The authors are grateful to Hirokichi Tanaka, staff researcher of Group One of the National Institute for Researches in Inorganic Materials, Tokyo, and to Prof. Hiroshige Suzuki of Tokyo Institute of Technology for their valuable discussions during the course of the present study.

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